Displacement of Chloride under the *Trans*-Effect of Strong σ-Donor Groups in Pt(II) Complexes

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The kinetics of the reactions:

trans-$[PtL_2(R)Cl]$ + Y^- → trans-$[PtL_2(R)Y]$ + Cl^-
(R = H, C_2H_5, m-$CF_3C_6H_4$, C_6F_5; L = $P(C_2H_5)_3$; Y^- = Br^-, I^-, N_3^-, NO_2^-, CN^-, SCN^-, thiourea) in CH_3OH at 25 °C are described. The pseudo-first-order rate constants fit the usual two-term rate law, $k_{obs} = k_1 + k_2[Y^-]$, with the k_2 term strongly depending on the entering group Y^-. To the extent that the term k_1 can be taken as a measure of trans *effect, this is found to parallel the* trans-influence *order of R, H > C_2H_5 > m-$CF_3C_6H_4$ > C_6F_5. This suggests a mechanism wherein the weakening of the Pt–Cl bond* trans *to strong σ donors R in the ground state is the driving force of the bimolecular reaction with a weak nucleophile which is devoid of π acceptor ability, such as methanol (ground state σ-trans-effect).*

When Y^- has good π acceptor abilities, contribution from the k_2 term becomes predominant, indicating that the driving force of the reaction is now the stabilization of the 5-coordinate transition state (transition state π - trans- effect).

Introduction

Current views on the effect of a coordinate group on the rates of substitution of a ligand *trans* to it in Pt(II) complexes (*trans*-effect) [1] or on the strength of such a bond (*trans*-influence) [2] can be made to fit into a unitary picture when the group in question has strong σ donor properties. Such a group in fact, will (*i*) weaken the bond *trans* to it in the ground state (ground state σ *trans*-effect and *trans*-influence) and (*ii*) share a greater amount of metal *p* orbitals in the transition state than in the ground state (transi-

tion state σ-*trans*-effect) [3]. Both these mechanisms of bonding interaction suggest that in complexes of type *trans*-$[PtL_2(R)Cl]$ with R = strong σ donor ligand, the *trans*-effect order should parallel the *trans*-influence order. When the group R has strong π acceptor abilities (olefins, CO *etc.*), it can accelerate a substitution reaction by accommodating the excess electron charge induced on the metal by bimolecular attack by the entering group Y^- (transition state π-*trans*-effect) [4, 5].

Similar arguments apply also when, with a given R, Y^- has good π acceptor properties. In this case also the rate of substitution will be mainly governed by stabilization of the 5-coordinate transition state.

A systematic study of *trans*-effect is available for complexes of type *trans*-$[PtL_2(R)$ Cl], where R = Cl [6], CH_3 [7], C_6H_5 [7], m-FC_6H_4 [8], p-$NO_2C_6H_4$ [8], o-tolyl [9], mesityl [10], reacting with either such good nucleophiles as I^-, SCN^-, PhS^-, $S_2O_3^{2-}$ *etc.* or pyridine [11–13]. We have now extended the range of *trans*-groups in these complexes to include H, C_2H_5, m-$CF_3C_6H_4$, C_6F_5, in the reactions of chloride displacement by a variety of nucleophiles in methanol at 25 °C.

Experimental

The complexes *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R ref.: H [14]; C_2H_5 [15]; C_6F_5 [16]) were prepared by literature methods and characterized by elemental analysis and i.r. spectra.

trans-$[Pt(PEt_3)_2(m$-$CF_3C_6H_4)_2]$

cis-$[Pt(PEt_3)_2Cl_2]$ (1 g) suspended in dry benzene (20 ml) was treated with Grignard reagent prepared from magnesium (0.48 g), *m*-trifluoromethylbromo-benzene (2.8 ml), a trace of iodine, and diethyl-ether (30 ml). The mixture was stirred at 20 °C for 2

TABLE I. Observed First order-Rate Constants k_{obs}, s^{-1} for the Reaction of $[Pt(PEt_3)_2(R)Cl]$ Complexes with Various Reagents Y in Methanol at 25.0 °C.

Complex	Y	Y/[M]	k_{obs}/s^{-1}
trans-$[Pt(PEt_3)_2(H)Cl]$	NO_2^-	0.001	0.565
		0.005	0.566
		0.010	0.567
		0.030	0.576
		0.050	0.583
	Br^-	0.002	0.561
		0.010	0.565
		0.030	0.600
		0.060	0.626
		0.100	0.682
	N_3^-	0.002	0.562
		0.010	0.574
		0.030	0.598
		0.060	0.645
		0.100	0.710
	I^-	0.002	0.775
		0.010	1.15
		0.030	2.20
		0.060	3.43
		0.100	5.64
	SCN^-	0.001	0.595
		0.005	0.980
		0.020	4.60
		0.030	6.49
		0.050	10.5
	$SC(NH_2)_2$	0.0005	4.00
		0.0010	7.52
		0.0030	19.9
		0.0050	32.7
		0.0100	64.1
trans-$[Pt(PEt_3)_2(Et)Cl]$	N_3^-	0.005	4.82×10^{-2}
		0.010	5.14 "
		0.030	4.92 "
		0.050	4.62 "
		0.100	4.62 "
	SCN^-	0.001	4.88×10^{-2}
		0.005	4.65 "
		0.010	4.82 "
		0.025	4.86 "
		0.050	4.83 "
	$SC(NH_2)_2$	0.0010	5.71×10^{-2}
		0.0025	8.41 "
		0.0050	11.7 "
		0.0100	19.8 "
		0.0150	27.5 "
trans-$[Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)Cl]$	NO_2^-	0.005	2.82×10^{-3}
		0.010	3.01 "
		0.020	2.95 "
		0.050	2.89 "
		0.100	2.91 "
	N_3^-	0.0075	3.12×10^{-3}
		0.015	3.02 "
		0.030	3.15 "
		0.050	3.21 "
		0.100	3.11 "
	Br^-	0.005	3.25×10^{-3}
		0.030	3.35 "

TABLE I. *(continued)*

Complex	Y	Y/[M]	k_{obs}/s^{-1}
		0.050	3.62 "
		0.075	3.70 "
		0.100	3.85 "
	I$^-$	0.0025	3.35 × 10^{-3}
		0.0062	3.53 "
		0.0120	3.70 "
		0.0250	4.25 "
		0.0500	5.40 "
	SC(NH$_2$)$_2$	0.001	6.1 × 10^{-3}
		0.002	9.3 "
		0.003	12.5 "
		0.005	19.3 "
		0.010	34.6 "
trans-[Pt(PEt$_3$)$_2$(C$_6$F$_5$)Cl]	N$_3^-$	0.005	2.05 × 10^{-5}
		0.030	2.25 "
		0.050	2.50 "
		0.100	2.91 "
	Br$^-$	0.005	2.15 × 10^{-5}
		0.030	2.40 "
		0.050	2.55 "
		0.100	3.05 "
		0.200	4.25 "
	I$^-$	0.005	4.21 × 10^{-5}
		0.050	16.1 "
		0.100	28.4 "
		0.150	41.2 "
		0.200	58.3 "
	SCN$^-$	0.005	2.90 × 10^{-5}
		0.020	6.00 "
		0.050	12.3 "
		0.100	21.5 "
	CN$^-$	0.001	1.15 × 10^{-3}
		0.002	2.12 "
		0.003	3.63 "
		0.005	5.82 "
		0.010	11.3 "
	SC(NH$_2$)$_2$	0.002	0.74 × 10^{-3}
		0.003	1.04 "
		0.005	1.88 "
		0.010	3.61 "
		0.020	7.02 "

hr, then hydrolyzed with ice and dilute hydrochloric acid. The crude product isolated from the organic layer by evaporation was chromatographed on alumina. Elution with light petroleum (bp 40–70 °C) afforded *trans*-[Pt(PEt$_3$)$_2$(*m*-CF$_3$C$_6$H$_4$)$_2$] as needles (0.36 g) from light petroleum, m.p. 165–167 °C. *Anal.* Found: C, 43.45; H, 5.37%. C$_{26}$H$_{38}$F$_6$P$_2$Pt requires C, 43.27; H, 5.30%.

trans-[Pt(PEt$_3$)$_2$(*m*-CF$_3$C$_6$H$_4$)Cl] was obtained by reacting a benzene solution of *trans*-[Pt(PEt$_3$)$_2$(*m*-CF$_3$C$_6$H$_4$)$_2$] with hydrochloric acid in ether in the ratio 1:1. The mixture was allowed to react under magnetic stirring for 4 days at room temperature. After evaporation of the solvent the product was crystallized from methanol giving colourless crystals, m.p. 82–84 °C. *Anal.* Found: C, 37.22; H, 5.54%. C$_{19}$H$_{34}$P$_2$F$_3$ClPt requires C, 37.28; H, 5.60%.

The infrared spectrum of this complex shows a medium–strong Pt–Cl stretching band at 273 cm^{-1} (Nujol mull). All the other products were of reagent grade and were used without further purification. Methanol was distilled over magnesium methoxide.

Kinetics

Slower reactions were followed spectrophotometrically by measuring spectral changes of the reaction mixture with time in the range 320–220 nm by means of an OPTICA CF 4 recording spectrophoto-

TABLE II. First-order (k_1/s^{-1}) and Second-order $(k_2/s^{-1} \text{ mol } M^{-1})$ Rate Constants for the Reactions of $[Pt(PEt_3)_2(R)Cl]$ Complexes with Several Entering Groups in Methanol at 25 °C.

| Complex	k_1	Second-order Rate Constant k_2 for Entering Reagent Y						
		$Y:NO_2^-$	N_3^-	Br^-	I^-	SCN^-	CN^-	$SC(NH_2)_2$
trans-$[Pt(PEt_3)_2(H)Cl]$	0.560	0.38	1.505	1.235	49.00	296		6310
trans-$[Pt(PEt_3)_2(Et)Cl]$	0.048		–			–		15.5
trans-$[Pt(PEt_3)_2(mCF_3C_6H_4)Cl]$	0.003	–	–	0.0065	0.043			3.17
trans-$[Pt(PEt_3)_2(C_6F_5)Cl]$	0.00002		0.000092	0.0001	0.00272	0.00196	1.13	0.350

meter and, at a fixed wavelength, by using a Beckman D.U. instrument equipped with a Saitron 301 photometer and a Servogor 5 recording potentiometer.

The reactions were started by mixing known volumes of pre-thermostatted standard solutions of reagents in the thermostatted (±0.1 °C) cell compartment of the spectrophotometer. The nucleophile was present in sufficient excess to ensure pseudo first-order conditions and to force the reactions to go to completion.

Faster reactions were followed by means of a Durrum Gibson D 110 stopped-flow apparatus with a 20 mm observation cell. A Tektronics model 564 storage oscilloscope equipped with a Polaroid camera was used to record the data. The values of rate constants, k_{obs}, listed in Table I were obtained from the slopes of plots of $\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the optical densities of the mixture at time t and after 7–8 half-lives, respectively. Final spectra were compared with those of original samples independently prepared. The values of k_{obs} were reproducible to better than ±10%. The effect of ionic strength on the rate of these reactions proved to be negligible.

Results and Discussion

The reactions:

$$trans\text{-}[PtL_2(R)Cl] + Y^- \longrightarrow$$

$$trans\text{-}[PtL_2(R)Y] + Cl^- \qquad (1)$$
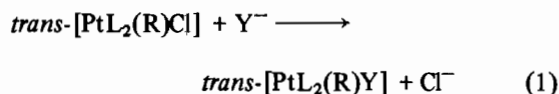
(R = H, C_2H_5, $m\text{-}CF_3C_6H_4$, C_6F_5; $Y^- = Br^-$, I^-, N_3^-, NO_2^-, CN^-, SCN^-, thiourea) at 25 °C in methanol under pseudo-first-order conditions (excess of nucleophile) are virtually quantitative and obey the two-term rate law:

$$k_{obs} = k_1 + k_2[Y^-] \qquad (2)$$

In many cases the k_2 term was either statistically insignificant in the 0.001–0.1 M Y^- concentration range (Table I and II) or its contribution to k_{obs} was rather small. A definite second order contribu-

tion was always observed in the reaction of all the substrates with $Y^- = CN^-$ and thiourea.

Solvolytic Pathway

In the nucleophile-independent path, the solvated intermediate formed by reversible release of chloride is rapidly and quantitatively scavenged by Y^- to form the reaction product:

$$(3)$$
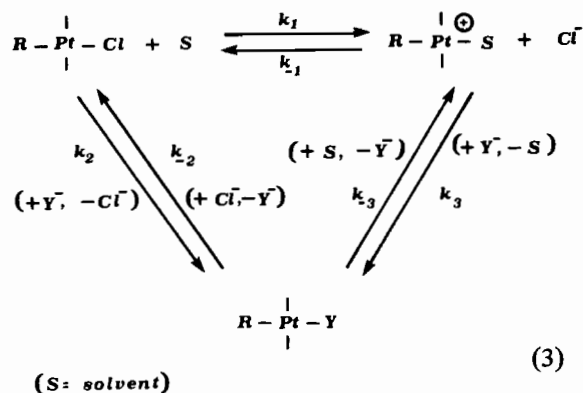
Therefore the kinetic scheme (3) reduces to rate law (2).

We have already shown that when the entering group Y is a substituted pyridine and R = C_6H_5, o-tolyl, and mesityl, substitution takes place by the solvent path only, and an equilibrium is reached [12, 13]. When the entering group competes more effectively with the chloride for the solvento intermediate, i.e., $k_3[Y^-] \gg k_{-1}[Cl^-]$, the reaction goes to completion $(k_{-3} = 0)$ and is controlled by the k_1 path. The predominance of the k_1 path in these reactions is a consequence of the poor discriminating ability of these substrates.

If the k_1 values can be reasonably assumed as a measure of the trans-effect of σ donor ligands, they are seen to correlate fairly well with trans-influence, in the order of R: H > $CH_3 \cong C_2H_5 > C_6H_5 > m\text{-}CF_3C_6H_4 \cong m\text{-}FC_6H_4 \cong p\text{-}NO_2C_6H_4 > o\text{-}tolyl > $ mesityl > C_6F_5, including all available literature data. The difference in reactivity spans a range of 6 orders of magnitude. The position of o-tolyl and mesityl is mainly due to steric reasons. Likewise the penta-fluorophenyl complex owes part of its reduced reac-
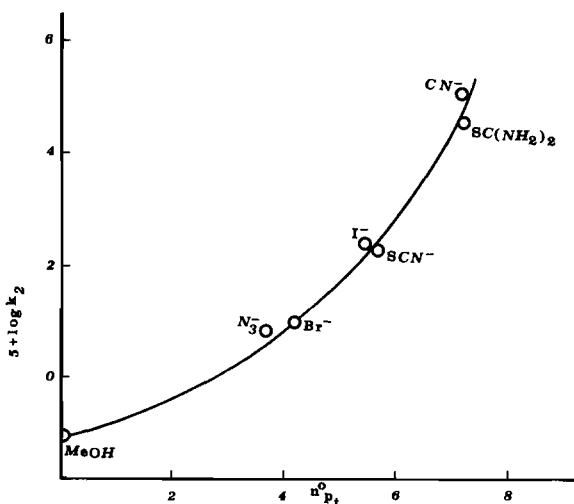
Fig. 1. Correlation of the rates of reaction of *trans*-[Pt-(PEt₃)₂(C₆F₅)Cl] with the n_{Pt}^o values of several nucleophiles.

Fig. 2. Correlation of the rates of reaction of *trans*-[Pt-(PEt₃)₂ (*m*-CF₃C₆H₄)Cl] with the n_{Pt}^o values of different nucleophiles.

tivity to steric strain produced above and below the square plane of the complex by the *ortho* fluoro substituents on the aromatic ring. However, the main effect seems to be due to electron withdrawing on the molecular σ bonding framework and strengthening of the Pt–Cl bond.

It appears that steric hindrance and inductive electron release by tue R group along the R–Pt–Cl axis hinder the attack by σ donor nucleophiles, enhance the capacity of the small and neutral solvent molecules as nucleophiles, produce a high intrinsic reactivity and low discriminating ability of the substrates. The mechanism can be described as one in which bond breaking is predominant over bond making, with the activation process requiring very weak bond both with the entering and the leaving group.

Nucleophile-dependent Pathway

The reactions of all substrates with CN⁻ and/or thiourea show a well defined dependence on the nucleophile concentration. These nucleophiles are known to possess good π acceptor properties and to stabilize the 5-coordinate transition state in reactions with Pt(II) substrates *via* electron delocalization [17]. The role of the π acceptor properties of the entering nucleophile is enhanced by strong σ donation by a *trans* R group in the ground state, *via* expansion of the 5d Pt(II) orbitals which makes them more available for overlap with empty orbitals of the incoming, biphilic ligand (transition state π-*trans*-effect).

As a matter of fact, the *trans*-effect order for the reactions with thiourea is the same as that observed for the poor nucleophile methanol (k_1 values), confirming that the same inductive electron release effect by the ligand R dictates the reactivity for both
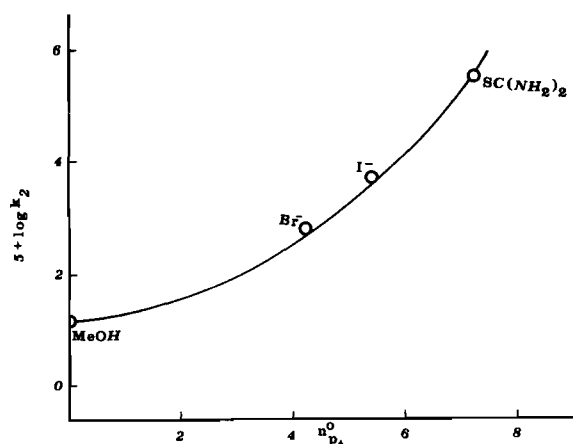
k_1 and k_2 pathways, even through two distinct activation processes. These involve destabilization of the ground state with poor nucleophiles (such as the solvent) and stabilization of the transition state when good entering groups are involved. In other terms, when strong σ donor groups are present in *trans* position to the ligand being displaced, different activation paths can be operative depending on the bonding properties of the incoming nucleophiles. Therefore, this provides a rationale for the finding that in this homogeneous class of Pt(II) substrates large deviations are observed from a simple LFER when the customary set of nucleophilic reactivity constants, n_{Pt}^o, are used. In fact, these were obtained from reactivity data pertaining to the standard substrate *trans*-[Pt(pyridine)₂Cl₂], where the ligand *trans* to the chloride being displaced has very weak σ donor ability. Thus, plots of lg k_2 for *trans*-[PtL₂(R)Cl] (R = C₆F₅ and *m*-CF₃C₆H₄) *versus* n_{Pt}^o as defined above show that the reactivity of π bonding nucleophiles (*i.e.* thiourea) is higher than expected from a simple linear relationship (Figs. 1 and 2).

Summing up, the use of strong σ donors as *trans* ligands will allow, through the agency of different activation processes, to discriminate between σ donor and π acceptor biphilic entering nucleophiles, by enhancing the intrinsic reactivity of the latter.

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